

**ANTI-MICROBIAL PACKAGING MATERIALS AND METHODS
FOR MAKING THE SAME**

Cross-Reference to Related Applications

[0001] This application is a continuation-in-part of US Patent Application Serial No. 10/003,799, filed November 2, 2001, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention pertains to polymer dispersions containing anti-microbial zeolites. The stable, zeolite-containing dispersions may be formulated in water-based or solvent-based systems and can be used on food packaging films. The invention also pertains to methods of applying an anti-microbial coating onto packaging materials.

BACKGROUND OF THE INVENTION

[0003] Anti-microbial packaging is of increasing importance in the food industry. Anti-microbial packaging allows manufacturers to distribute products with longer shelf lives, which permits the manufacturer to decrease distribution costs. Anti-microbial packaging also enables both the merchant and the consumer to stockpile products. This permits the manufacturer to increase sales volume. Anti-microbial packaging also provides some assurance against intentional and unintentional contamination. Additionally, it is speculated that manufacturers who utilize anti-microbial packaging will see their products purchased in preference to other brands which lack anti-microbial packaging. Lastly, the ability to protect foods longer may permit a transition to fresher food products, transforming the market and establishing new brands.

[0004] Various anti-microbial agents have been used with packaging materials. Examples of anti-microbial agents used in paper and plastic food packaging materials include alcohols and organic acids such as acetic, propionic, benzoic and sorbic acids. Organic acid salts have been employed as well. Examples include potassium and calcium sorbates, sodium benzoate and quaternary salts. Organic acid anhydrides such as sorbic acid anhydride, and benzoic acid anhydrides have also been employed. Polymeric anti-microbial materials such as hexyl-PVP have also been suggested for use as packaging materials. Another suggested category

of anti-microbials are inorganic anti-microbials, examples of which include sulfites, nitrites, chlorides, carbon dioxide, sulphur dioxide and silver salts.

[0005] These anti-microbial materials have been added to packaging materials in a variety of ways. In some of the simplest applications, anti-microbials have been dusted in or sprayed on packaging materials. However, anti-microbial agents that are not attached to the packaging material may leech from the package surface. For food products in particular, leeching of the anti-microbial agent is not desirable as it may lead to ingestion of the anti-microbial. These anti-microbial treatments are also subject to wear, and typically lose effectiveness with time and handling. For long-term anti-infective properties, it has been suggested that the anti-microbial agent be incorporated into the raw material from which the packaging material will be made. In so doing, however, much of the anti-microbial agent is “buried” within the packaging material. Though the buried anti-microbial will “ride with” the package, and thus serve some preventative role, it will not be available for the first line of defense at the packaging surface. The amount of buried, wasted anti-microbial agent in molded or extruded packaging materials is especially high.

[0006] One of the difficulties encountered with producing anti-microbial or microbially resistant packaging materials is the cost of the anti-microbial agent. Anti-microbial agents, typically, are more expensive than the paper and/or plastic material that forms the remainder of the packaging. Another difficulty is the cost associated with incorporating the specific anti-microbial agent into the packaging material. For certain products, particularly food products, the cost of anti-microbial packaging materials has been prohibitive. With the growing emphasis on the importance of anti-microbial properties, longer-acting, more expensive anti-microbial agents are being developed. Zeolites are a preferred, long-acting anti-microbial agent, but they are quite expensive. It would be highly desirable to be able to use zeolites as part of a more cost effective anti-microbial coating.

[0007] It has been suggested to use anti-microbial zeolites to render polymeric resins anti-microbial. Specifically, U.S. Patent No. 4,938,958 discloses “incorporating the antibiotic zeolite into the resin by means of kneading it with the zeolite or coating the antibiotic zeolites on the surface of such a resin” (col. 4, lines 34-39). No further description of coating is offered. No level of addition is offered. It is not stated that the addition is made to molten resin, or with wet or dry zeolites. No suggestion of forming a coating solution is given. This patent also suggests directly mixing zeolites with paints to impart antibiotic properties, or coating the zeolite on the surface of the coated films” (col. 4., lines 56-65). Again, there is no description of how to coat

and no instruction as to how to convert the paints to formulations that can be easily and inexpensively combined with packaging materials, such as clear plastic film, to render them anti-microbial.

[0008] Recently, there have been suggestions to put silver-containing zeolites into plastic films, which are a preferred packaging material for food. For example, in Food Contact Substance Notification FCN 000047, the Food and Drug Administration has approved Zeolite A made by Sinanen Company Ltd. for use in all types of food contacting polymers, in a level of up to 5%. However, films are typically made by extrusion processes, and for the reasons given above, anti-microbial agents may be buried in an extrusion product. This is especially true for films, as the heat which causes the flow of the film-former also creates a skin of film-former at the surface, which blocks the anti-microbial agent from the surface. However, packaging films are water-repellant (hydrophobic) and are typically produced by the extrusion process, and for the reasons given above, anti-microbial agents may be buried within the hydrophobic product. Since the performance of the anti-microbial agent depends on mobility through a moisture medium, the extruded hydrophobic polymer limits the anti-microbial effectiveness since it reduces the anti-microbial mobility. Thus, a substantial amount of the zeolite near the surface is covered and therefore unavailable for its intended purpose. The result is a film that is expensive to manufacture and less effective than desired.

[0009] One specific attempt to incorporate anti-microbial zeolites into films and the like is found in U.S. Patent No. 5,556,699, (the '699 patent). The '699 patent discloses preparing "antibiotic" films by admixing the zeolites and a variety of polymer materials, (see column 4, lines 24-44) in the usual manner and forming the films by any known method such as casting, extrusion (inflation, T-die, calendering, cutting), and drawing methods (see col. 4 lines 45-58). In addition, the patent discloses laminates made from such films, by co-extrusion, or laminating (col. 5, lines 12-14). Examples 1-3 and 5 demonstrate co-extrusion. Example 4 describes using a mixture of polyurethane and zeolites to coat a substrate used in the manufacture of a toothbrush, prior to the addition of the bristles. See col. 9, line 26. Despite this disclosure, further improvements in coating methods and processes, and in zeolite coating formulations, have been sought. For example, in the past, it was known that the zeolites would rather quickly settle at the bottom of the vessel. Thus, the actual coating applied to the surface would often contain far less of the anti-microbial than desired. The effectiveness of the anti-microbial activity was also less than expected.

[0010] More sophisticated mechanisms for incorporation of anti-microbials into packaging are also being developed. U.S. Patent No. 6,264,936 B1 discloses a non-leeching, long acting, anti-microbial coating, which kills microorganisms on contact. The coating has particular importance for the inside surface of bottles containing ocular solutions. The coating comprises a polymer matrix made up of arms or tentacles of the polymer, and a biocide contained in reservoirs held within a swirl of tentacles, and attached, one molecule at a time, to the tentacles. The polymer material "must be capable of insinuating the biocide into the cell membrane of the microorganism". Thus, the biocide is released "into the microorganism but not into the surrounding environment" (See col. 2, lines 49-59).

[0011] The use of printing apparatus to apply materials other than ink onto various materials is known. For example, artisans use printing apparatus to apply spot gloss coatings. Such techniques, however, are completely unrelated to the zeolite extrusion or kneading processes described above. Moreover they provide no guidance concerning the use of printing techniques to apply zeolite-containing film coating dispersions. In fact, it has been found that many zeolite-containing dispersions cannot be satisfactorily applied with printing apparatus. One cannot arbitrarily or haphazardly combine acrylic or non-acrylic polymers and zeolites together and produce aqueous dispersions that are stable and ultimately printable. For example, many dispersions have a neutral or acidic pH to facilitate ion release from the zeolites and/or include polymers having acid numbers over 200, mainly to enhance solubility which, in turn, enhances film forming properties. It has been found, however, that water-based dispersions having such pH's and higher acid number polymers are unstable. Metal ions from the zeolite such as silver interact with acidic groups on the polymer and form a complex that precipitates and causes the viscosity of the dispersion to increase to the point where the dispersion cannot be readily applied i.e. printed onto a substrate.

[0012] Packaging materials are typically made by converters, who construct the materials from existing paper or plastic stock. Converters typically run printing, scoring, laminating and folding operations, which operate at room temperature. Their profits depend on their application of these processes to the starting materials. Imparting anti-microbial properties to packaging materials has heretofore required additional production machinery, such as heated extrusion equipment. In spite of the desire of their customers to have packaging materials with long-term anti-microbial properties, converters have been unable to deliver such a product at an economical price especially for those using zeolites. Even though anti-microbial packaging commands a higher price, it has been cost prohibitive to date for converters to add the necessary equipment to produce the desired anti-microbial packaging materials. With the present invention, this

advantage may be economically realized on existing converter equipment, while maintaining other expected properties in packaging materials, such as scratch resistance and handling resistance.

SUMMARY OF THE INVENTION

[0013] In accordance with one preferred aspect of the invention there is provided a zeolite-containing dispersion which contains a) a polymer having an acid number of less than about 200, and b) from about 0.5% to about 10% by weight zeolites containing anti-microbial metal ions such as silver. The zeolites selected have a particle size of between about 2 and about 7 microns and a pore size of between about 3 and about 5 Angstroms. Although the dispersion can be water or solvent-based, some preferred embodiments include water-based dispersions having not only the polymers described above but also have a pH of greater than or equal to about 9 but less than about 9.7.

[0014] In another aspect there is provided a method of applying an anti-microbial treatment to a surface of a packaging material. The method includes a) providing a zeolite-containing dispersion as described above, b) printing the dispersion onto the surface of the packaging material, and c) allowing the dispersion to dry thereon. The resultant product is a packaging material having a dried, zeolite-containing coating layer on at least a portion thereof. Other aspects of the invention include packaging materials having anti-microbial properties on at least one surface thereof as a result of the inventive dispersion being applied thereto. In these aspects of the invention, the zeolites preferably comprise from about 1% to about 5% by weight of the dried coating layer.

[0015] In still further aspects of the invention, there are provided 1) methods for rendering paper or a paperboard substrate anti-microbial or otherwise more resistant to bacteria by applying a water-based or solvent-based polymer-zeolite dispersion as described herein to the substrate, and 2) methods for rendering a nylon, polyester or polystyrene film anti-microbial or more resistant to bacteria by applying a water-based or solvent-based inventive dispersion to the film.

[0016] The dispersions of the present invention may be applied using conventional printing equipment such as rotogravure printing apparatus, at ambient temperatures. As a result, the present invention provides a relatively inexpensive but quite versatile method for achieving anti-microbial coatings on packaging materials. The dispersions employed in the methods of the

present invention are relatively low viscosity, enabling them to be easily handled by printing equipment. The dispersions, whether water or solvent-based, are also very stable, yielding a uniform distribution of zeolites in the printed coating layer. While Applicant does not wish to be bound by any particular theory, it is believed that the zeolite particles contribute at least in part to the stability of the dispersion, and ensure uniform, high levels of zeolites in the coating layer. Moreover, by limiting the polymers to those described herein, i.e. those having an acid number of less than about 200, and, in the case of water-based embodiments, by further maintaining the pH of the dispersions at or above 9, it has been surprisingly found that the precipitation and stability problems of the prior art are avoided.

[0017] One advantage afforded by the present invention is the fact that the artisan can more efficiently deliver an effective amount of the anti-microbial zeolite to the exterior surface of the coating layer. This is to be contrasted with the previously described zeolite containing coatings wherein the zeolites were forced below the surface and consequently unavailable for surface anti-microbial effect on the packaging materials. Indeed, although the silver forms no more than about 2.5% by weight of the preferred zeolite, the anti-microbial effective levels of silver is less than about 0.001% by weight of the dried coating.

[0018] The anti-microbial dispersion formulations of the present application may also provide scratch resistance and handling resistance, which are especially important in food contact films.

[0019] The anti-microbial dispersion formulations of the present invention may also incorporate a variety of other coating ingredients. For example, ink pigments for lithography, rotogravure printing, flexography, and offset gravure printing may be incorporated into the coating formulations. Additional anti-microbial agents such as ZnO can be included. Thus, the application methods may also include discontinuous, patterned, printing, or full cover printing, which extends continuously across a surface portion of the packaging material.

[0020] Other and further advantages of the present invention will become apparent to artisan of ordinary skill upon reading the specification and claims attached hereto with reference being made to the attached figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] Figure 1 is a schematic representation of a zeolite used in the present invention.

5 [0022] Figure 2 is a schematic representation of a cross-section of an anti-microbial surface formed by a coating dispersion of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

10 [0023] The solvent-based and water-based novel anti-microbial dispersion formulations are described herein in relation to food contacting films. This is in no way intended to limit the application of the dispersions and coatings achieved therewith. The use of singular terms for convenience in the description is in no way intended to be limiting. Thus, for example, a formulation described as comprising "an anti-microbial" includes reference to a formulation
15 comprising one or more of such anti-microbials; and the description of "a packaging material with a coating" includes reference to one or a number of coatings, at least one of which may be the dried anti-microbial coating layer described herein. The invention is also not limited to the particular process steps or materials disclosed herein, as such process steps and materials may vary somewhat. The terminology employed herein is used for the purpose of describing particular
20 embodiments only and is not intended to be limiting, since the scope of the present invention will be limited only by the appended claims and equivalents thereof.

[0024] For the purposes of the present invention, "substantially inert" shall be understood to mean that the inventive dispersions and the ingredients included therein, e.g. the polymers and
25 zeolites, etc., are not appreciably reactive with each other and do not cause or undergo significant precipitation or agglomeration. Furthermore, for this purpose, "significant" shall be understood to mean an amount greater than that which renders the coating dispersions unprintable using the apparatus described therein.

30 [0025] As pointed out above in the Summary of the Invention section, one preferred aspect of the invention includes a method of applying an anti-microbial treatment to a portion of a surface of a packaging material. The method includes the steps of providing a dispersion containing a polymer and zeolites containing silver ions wherein the zeolites have a particle size of between about 2 and about 5 microns, a pore size of between about 3 and about 5 Angstroms.
35 The dispersion is then applied as a coating to at least a portion of a surface of the packaging material, preferably by printing as described in detail herein. The coating is permitted to be dried

to form a coating layer having a surface in contact with the packaging material and an exposed surface which contains the polymer and zeolites on at least a portion thereof. The phrase “exposed surface” is intended to refer to the surface of the dried coating layer which becomes exposed to the environment, i.e. outer surface, and not the hidden (inner) surface that abuts the surface of the packaging material.

[0026] The liquid dispersions of the present invention preferably have a viscosity between about 10 and about 400 centipoise at 10- 25 °C. In more preferred aspects, viscosity of the dispersions are between about 200 and about 300 centipoise at 10- 25 °C. However, the viscosity and rheology can be modified so that the antimicrobial ink or coating can be applied by various printing and coating methods.

[0027] The zeolites used in the claimed process preferably have a particle size of between about 2 and about 7 microns and a pore size of between 3 and 5 Angstroms. In especially preferred aspects of the invention, the zeolites have a particle size of between about 4 and 6 microns and a pore size of at least about 4 Angstroms.

[0028] In these aspects of the invention, the zeolites make up from 0.5 % to 10% by weight of the dispersion. Preferably, the zeolites comprise from 1% to 5% by weight of the dispersion while most preferably the zeolites comprise from about 2% to about 5% by weight of the dispersion.

Dispersion Ingredients

[0029] One preferred aspect of the invention provides zeolite-containing dispersions, comprising:

- a) a polymer having an acid number of less than about 200; and
- b) from about 0.5% to about 10% by weight zeolites containing anti-microbial metal ions.

The zeolites are selected to have a particle size of between about 2 and about 7 microns and a pore size of between about 3 and about 5 Angstroms.

Polymers for Solvent-based Dispersions

[0030] A wide variety of polymers can be employed as part of the inventive dispersions. For example, a non-limiting list of the polymers that may be used in making the solvent-based formulations of the present invention includes, for example, polyamides, acrylics, polyurethanes, ethyl cellulose, polyvinylbutyral, polyketones and nitrocelluloses. Preferably, the polymers are

acrylics or nitrocellulose resins such as those having an acid number <2, RS type, ¼ sec, or other such resins having excellent solubility in alcohol. The nitrocellulose resin can also be modified to improve flexibility with a polyamide resin having a low acid number and low viscosity characteristics.

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[0031] Generally, however, suitable polymers which are otherwise well suited for the purpose of being used as part of a film coating can be employed. Many solvent-based dispersions according to the present invention may be made with acrylic polymers. In one example, a polyamide is added to the acrylic polymer, and often a third resin is included. These formulations produce particularly adherent anti-microbial coatings. For example, they can be made to adhere to low energy polyethylene film. The solvent-based coating of the present invention also provides good adhesion to paper, nylon, and corona treated polyethylene. Films to which an anti-microbial dried coating layer of zeolites may be applied, may be alcohol based, and heat sealable, and are easily rendered non-fogging. Some particularly preferred polymers include polyamides available under the trade name UNI-REZ[®] and available from Arizona Chemical, Savannah, GA.

[0032] Additional resin binders useful in making 1% and 2% solvent-based dispersion formulations are SS Nitrocellulose Methyl methacrylate copolymer and SS Nitrocellulose. Formulations of Methyl methacrylate copolymerized rosin, and Polyvinyl chloride resin were stable at 5% by weight zeolites, and dip coated samples of these formulations onto polystyrene and stainless steel yielded an anti-microbially effective amount of silver ions.

Method of Making Solvent-based Anti-microbial Dispersions

[0033] The solvent-based dispersions may be formed as follows:

The resin is dissolved in an appropriate solvent(s), such as n-propyl alcohol, isopropyl alcohol, ethyl acetate or propylene glycol monomethylether. A variety of desired additives may then be added to the mixture, which is again stirred to assure uniform distribution of the ingredients. Next, zeolites are added and the mixture stirred vigorously until all ingredients are dispersed, i.e. for about another 30 minutes. The mixture is then passed through a horizontal mill which contains inert beads in the range of 0.5 – 2 mm to complete the break-up of zeolites agglomerates that form during shipping or storage, and to remove the air from the surface of the zeolite, so it may be more easily wetted and enter into the dispersion. Optionally, a wax may be added and the mixture again stirred until evenly distributed, i.e. for about 30 minutes. The product is then filtered through 10-25 micron filter and packed in suitable containers.

[0034] Such coating formulations retain great stability. Although some settling of the zeolite may occur in diverse conditions such as prolonged storage, mere stirring of the formulation before beginning the application process will easily yield a uniform dispersion of zeolites that remains stable through out the application process.

[0035] It will be understood by those of ordinary skill that the foregoing represents a general description of how the dispersions are formed. The exact amount of time required for each mixing step, for example, will depend upon several factors, including but not limited to specific resins selected, batch size, apparatus employed, optional ingredients employed, etc.

Polymers for Water-based Dispersions

[0036] The printable dispersions can also be a water-based dispersion. In such instances, a non-limiting list of suitable polymers includes sulfonated polyesters, maleics, shellacs and acrylics, with acrylics such as Joncryl styrene-acrylic resins or Lucidene being preferred. In particularly preferred embodiments, the polymer is an acrylic emulsion such as Joncryl DFC 3030, which has an acid number of 64, or Joncryl DFC 3040, which has an acid number of 55. These are emulsions containing polymers with low acid numbers and low to medium Tg (i.e. softening points) which allow for good film formation on films as well as paper substrates. Other acrylic polymers will be apparent to the artisan so long as they have an acid number of less than 200, preferably less than about 80, and more preferably less than about 70. In most aspects of the invention, the polymer comprises up to about 60 % by wt of the dispersion but will usually be in the range of 30-60% by wt.

Method of Making Water-based Anti-microbial Dispersions

[0037] The method of making the water-based dispersions, other than using water rather than organic solvents, is not substantially different from the steps followed to make the solvent-based dispersions of the present invention and will be apparent to the ordinary skilled artisan without undue experimentation.

[0038] The polymers for both the solvent-based and water-based formulations are chosen such that the dried coating layers are substantially hydrophobic and not easily dissolved in water. This provides for water resistance which is required in most packaging applications. The zeolites remain at the exposed surface of the coating layer and continue to provide the anti-microbial property for substantially the full life of the packaging material. Such alkali soluble acrylic resins are available from acrylic polymer suppliers, such as, SC Johnson in Racine, WI., under the trade name Joncryl, as well as Rohm and Haas, Philadelphia, PA, under the trade name,

Morez (formerly Morton International). Preferred acrylic emulsions that have shown stability in formulations with 1-2% silver zeolite typically have acid numbers ranging 45 -192 and molecular weights above 100,000. Examples include those available from SC Johnson (Joncryn), and Rohm and Haas (Lucedene), (formerly Morton International).

E. Zeolites

[0039] Zeolites are aluminosilicates. They have a crystalline structure which permits them to incorporate a variety of substances. Naturally occurring zeolites contain either sodium or calcium, or both, and are generally represented by the formula $\text{Na}_2\text{O} \bullet \text{Al}_2\text{O}_3 \bullet x \text{SiO}_2 \bullet x \text{H}_2\text{O}$.

Synthetic zeolites may contain potassium, magnesium, and iron. Zeolites undergo ion exchanges and the anti-microbial zeolites used in the present invention are those in which anti-microbial metal ions have been exchanged for other ions in the zeolite. Anti-microbial Zeolite release anti-microbial metal ions through the process of ion exchange and thus impart anti-microbial properties to the coating and the packaging material. The zeolites are dispersed as a fine solid in the dispersions. The most preferred antibiotic ion is silver, i.e. Ag^+ , however, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium and thallium ions are anti-microbial ions which may be used to create anti-microbial films according the present invention. The sodium, calcium, potassium and/or iron ions of the zeolite are exchanged for anti-microbial metal ions, e.g. silver ions, (Ag^+), to produce an anti-microbial zeolite.

[0040] Though the remainder of the description will refer to silver-containing zeolites, it will be understood that any anti-microbial metal ion-containing zeolite may be used in the present invention. Zeolite, type A, a synthetic aluminosilicate, manufactured by Sinanen Company, Ltd, and supplied by Agion, is one particularly preferred zeolite for purposes of the present invention and is depicted at 10 in Figure 1.

[0041] In Zeolite type A, silver, zinc and ammonium ions have been exchanged for the sodium ions. The silver in the zeolite does not typically exceed about 2.5% by weight. The free silver ions create an anti-microbial region at the surface of the coating, as shown in Figure 2, incorporate silver ions, 12. The zeolites used in the present application typically have a particle size of between 2 and 6 microns, and preferably between 4 and 5 microns. Most preferred are type AJ10D zeolites having a particle size of about 5 microns, and a pore size of about 4 Angstroms, permitting the silver ions to be readily released from the zeolite simply by contact with moisture. The zeolites generally comprise from about 0.5 to about 10% by weight of the dispersion but are preferably from about 1% or 2% to about 5% by weight of the dispersion.

Optional Dispersion Ingredients

[0042] The dispersions of the present invention can also contain one or more optional ingredients to improve its utility or confer additional properties to the final product. For example, preferred embodiments, the dispersion can include up to about 2 % by weight zinc oxide.

Packaging Substrates for Anti-microbial Dispersion Formulation Application

[0043] A non-limiting list of the film packaging materials that would be suitable for application of the anti-microbial dispersion formulations of the present invention include the following:

Cellophanes (plain & coated)	Vinyl Chloride Co-polymers
Cellulose Acetate Films	Vinylidene Chloride Co-polymers
Ethyl Cellulose	Aluminum Foils
Methyl Cellulose	Laminates
Polyesters	Paper
Polyethylene	Paperboard
Polypropylene	Glassine
Polystyrene	Nylon

[0044] Food packaging films suitable for use in the present invention include polymeric films such as blown film, oriented film, stretch and shrink film, heat shrinkable bags and food casings. "Food packaging films" as that term is used herein are flexible sheet materials which are suitably 15 mils or less and preferably less than 10 mils (250 microns) in thickness. Suitable films include regenerated cellulose and thermoplastic stretch or shrink films, and may be monolayer or multilayer films. Shrink films are preferably formed into heat shrinkable, biaxially oriented bags. Plastics such as homopolymers or copolymers of polyolefin's e.g. polypropylene, polyethylene, or polyamides, polyethylene terephthalate, polyvinylidene chloride copolymers or ethylene-vinyl acetate copolymers may also be used to form the food-contacting films of the present invention.

[0045] There are many methods for applying the dispersion formulations of the present application, however, printing is preferred. "Printing" as defined here is the delivery of an ink or coating at the desired thickness and image pattern onto a surface. Readily available printing

methods include low viscosity applications, such as rotogravure, flexography, screen, pad and offset gravure, while higher viscosity applications can include offset, lithography, and roll coating. The specific printing technique to be used for the antimicrobial coating depends on the desired package material and design. Films such as polyethylene would be printed by flexography using a central impression drum to support the film web, heavy guage paper can be printed by conventional rotogravure.

[0046] Rotogravure printing is the preferred embodiment in the method for applying the dispersion coating of the present invention. Gravure processes begin with the engraving of the desired pattern or image into a plate, or about a roller. The use of a roller provides for a continuous process, printing the image repeatedly onto a moving web. Thus, in the continuous process, deemed a rotogravure process, the print image desired is carved into the surface of the roller, sometimes called a print or engraved cylinder. The printing ink or zeolite dispersion is provided in a trough. The rotating cylinder is mounted horizontally such that, a full height of the cylinder extends into the print solution in the trough. As the cylinder turns, it is flooded with print solution. A doctor blade, extending the height of the cylinder removes the excess dispersion solutions, leaving the dispersion in the carved image. The cylinder then turns to a nip with an impression roller, and prints onto a web moving through the nip. Thus, an image is placed on the web.

[0047] In preferred aspects of the present invention, this rotogravure process and equipment are used to place a continuous or discontinuous pattern of the inventive anti-microbial dispersion on a continuously moving plastic film. The trough typically contains no mechanism to stir or agitate the print solution. On occasion, such as after shipment or storage, the dispersion of the present invention may require stirring before being placed in the trough, but no subsequent stirring mechanism is required. Simply by way of illustration, and without limitation, an antimicrobial coating can be applied via rotogravure. The first requirement is to adjust the coating viscosity to allow the coating to flow out uniformly on the substrate at the desired press speed. This viscosity adjustment is typically made by the addition of solvent to the desired viscosity. To assure there is no settling of the anti-microbial additive, the anti-microbial coating is stirred for a few minutes before being pumped into the gravure coating station. The coating is then applied using an engraved rotogravure cylinder equipped with a doctor blade. Once the coating is applied at the desired thickness, usually from about 3 to about 20 microns, it goes

through a thermal drying oven which removes the solvents and produces a dried antimicrobial film. After drying, the printed dispersion coating layer will have a thickness of from about 1 microns to about 12 microns, and preferably from about 2 microns to about 8 microns. In such processes, the dispersion may be applied to the packaging surface in either a continuous or discontinuous pattern, according to the needs of the artisan.

[0048] Although the dispersions of the present invention can be used with a variety of rotogravure printers, some specific printers in which the dispersions can be employed without modification thereto include such press producers as Mark Andy, Comoco, Bobst-Champlain, Schiavi, PCMC, Comexi and Windmoeller & Hoelscher (W&H). Depending on the apparatus selected, the dispersion can be printed on the packaging surface at a rate of from about 0.1 lbs./3,000 ft. square to about 2-3 lbs./3,000 ft. square.

[0049] The dispersions are particularly advantageous in printing applications, including silkscreen, offset gravure, lithographic and flexographic printing operations. More complicated or expensive equipment and processes may be used, if desired.

[0050] As stated above, films coated with the dispersions formulations of the present invention have a variety of uses, but perhaps the most important is as a food contacting film used both in food preparation and packaging, in both the commercial and home settings. However, the coating compositions of the present application have utility in any applications where anti-microbial surfaces are desired. For example, the coating could be used on the surfaces of the paper inserts for food container tops or lids, or on films or paper used for disposable sanitary covers, such as those for rolling pins, or dough preparing surfaces, or plastic bags used for food storage. In some preferred aspects, the film packaging materials to which the inventive dispersion is applied include polystyrene and polyurethane.

[0051] Thus the invention provides a novel dispersion and application method for providing an anti-microbial surface on a film, or other substrate. When dried, the dispersion yields a coating with zeolites at the surface, which will release silver ions upon the application of moisture. As shown on Figure 2, the coating composition, 20, is made up of base polymer, 22, with AgIONTM powder, 24, distributed there through. Exposure to air produces the surface film of moisture, 26, which provides for ion release at 28. The slow constant release of silver ions by the zeolite particles provides long-acting anti-microbial properties.

EXAMPLES

[0052] The following examples serve to provide further appreciation of the invention but are not meant in any way to restrict the effective scope of the invention.

5 Example 1 Aqueous Anti-microbial Coating

[0053] The following ingredients were combined to form a water-based, printable dispersion formulation according to the present invention:

	D.I. Water	1.90
	NH ₄ OH	1.00
10	Surfynol 420 (surfactant)	0.10
	n-Propanol	3.00
	Propylene glycol monomethyl ether (PGME)	4.00
	Lucidene 650 (acid no. 192)	80.0
	ZnO Solution	5.00
15	SST-3 Wax	3.00
	AgION AJ 10D	<u>2.00</u>
		100.00 parts by weight.

[0054] The coating formulation was prepared as follows:

- 20 1. 1.90 parts of de-ionized (D.I.) water, 1.00 part of ammonium hydroxide solution and 0.10 parts of Surfynol 420 to 80.00 parts of Lucidene 650 were combined with stirring and stirring was continued for 30 minutes.
2. Under constant stirring, 3.00 parts of n-propanol and 4.00 parts of PGME were added and stirring was continued for an additional 15 minutes.
- 25 3. Next, 5.00 parts of zinc oxide solution and 2.00 parts of AgION's AJ 10 D were added and the ingredients were stirred vigorously for an additional 30 minutes.
4. Next, the mixture of ingredients is passed through a horizontal mill having inert beads in the range of 0.5 – 2 mm diameter.
5. Finally, 3.00 parts of SST-3 wax were added and stirring was continued
- 30 for 30 minutes.

[0055] The resultant dispersion had a pH of 9.1 and was applied to polyethylene film via a Pamarco Hand Proofer using 180 (180 lines/inch) anilox roll and dried in an oven at 80°C for 10 minutes. The exposed surface of the resultant anti-microbial coating layer was found to have
35 the zeolites thereon.

Example 2

[0056] The treated substrates of Example 1 were next tested for anti-microbial activity against the following microbes:

Salmonella	Staphylococcus
E. coli	Yeast
Pseudomonas	Mold

[0057] These tests were performed by direct inoculation of a specific quantity of bacteria into a petri dish which contained a 2"x2" anti-microbial film sample and then quantifying the bacteria reduction using a control sample of film that did not contain the anti-microbial coating.

[0058] The quantification of the bacteria reduction in 24 hours is obtained from the following formula:

$$\% \text{ Reduction} = \text{CFU's / ml (of Assay + Control) @ T=0} - \text{CFU's / ml at T=24 hours}$$

$$\text{CFU's/ml (of Assay+Control) @T=0.}$$

In each case, the treated surfaces were determined to be 99.9% effective against each microbe.

Example 3

[0059] In this Example, the dispersion of Example 1 was applied to polystyrene film with #3 and #7 Meyer rods. The #3 rod produced a dry anti-microbial coating layer of about 3.75 microns, and the #7 rod, 8.75 microns. Two inch by two inch samples of the dried anti-microbial coating layer were treated with 25 ml. of 0.08% NaNO₃ to extract the silver ions. The #3 Meyer rods produced a sample that yielded about 503-506 mcg/L. silver ions. The #7 Meyer rods produced a sample that yielded 320 silver ions. The amount of silver ion available at the film surface is quite high and produces a very effective anti-microbial concentration. (A level of 50 µg/L of silver ions is considered a good level for anti-microbial effectiveness.)

Example 4 Aqueous Anti-microbial Coating

[0060] The following ingredients were combined to form a water-based, printable dispersion formulation according to the present invention:

Joncryl DFC 3030 (Acid NO. 64)	89.82
Purified Water	3.92
Isopropyl Alcohol	3.77

Silver Zeolite, AgION's AJ10D-M	2.12
Ammonium Hydroxide, Reagent	0.29
Dee Fo PI-12 defoamer	<u>0.08</u>
Total	100.00

[0061] Procedure:

1. 3.92 parts of de-ionized (D.I.) water, 0.29 parts of ammonium hydroxide solution, 0.08 parts of Dee Fo PI-12 and 89.82 parts of Joncryl DFC 3030 emulsion were combined and stirred for 30 minutes.

2. Under constant stirring, 3.77 parts of isopropanol is added and the mixture stirred for an additional 15 minutes.

3. Next, 2.12 parts of AgION's AJ10D-M were added and the ingredients stirred vigorously for an additional 30 minutes.

4. Next, the mixture of ingredients is passed through a horizontal mill having inert beads in the range of 0.5 – 2 mm diameter.

[0062] The process of Example 2 was repeated with this dispersion and the treated substrates were tested for anti-microbial activity against the following microbes:

E. coli	Mold
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These tests were performed by direct inoculation of a specific quantity of bacteria into a petri dish which contained a 2"x2" anti-microbial film sample and then quantifying the bacteria reduction using a control sample of film that did not contain the anti-microbial coating. In each case, the treated surfaces were determined to be 99.9% effective against each microbe.

Examples 5 and 6 Comparative

[0063] Type AJ zeolites were added to a styrenated acrylic soluble polymer and acrylic emulsion, at 1% (Example 5) and 2% (Example 6) by weight.

Example 5

[0064] To an acrylic composition containing a 7:1 ratio of Joncryl 80 emulsion (which has acid number of 60) and Joncryl 678 soluble resin (which has acid number of 215), pH 8.8 – 9.2, containing Zn was added 1% of AJ zeolite and the mixture was dispersed using a Red Devil Shaker for 6 minutes. The sample was left overnight and the dispersion had initial good flow properties. This sample was used to coat a test film and subsequently tested for anti-microbial effectiveness. It was found, however, that the dispersion became unstable upon further standing.

This is believed to occur due to the use of water soluble Joncryl 678 resin (Acid No. 215) at high pH causing the solution to become higher in viscosity and eventually caused settling of the resin as a metal complex. Levels of soluble Joncryl 678 in excess of about 1% causes the settling to occur more rapidly. If Joncryl 678 is removed from the formulation, the presence of Joncryl 80 (Acid No. 60) does not cause the settling to occur.

[0065] Similar results were obtained with soluble Joncryl DFC-3015 (Acid No. 240) and Joncryl DFC-3025 (Acid No. 220) resins in that they cause immediate settling when mixed with AJ zeolite material. No settling is observed when AJ zeolite is introduced into Joncryl DFC-3030 (Acid No. 64) or Joncryl DFC-3040 (Acid No. 55) emulsion.

Example 6

[0066] To the same acrylic composition of Example 5, was added 2% of AJ zeolite and the mixture was dispersed using a Red Devil Shaker for 6 minutes. This sample was left overnight and found to have increased in viscosity to where it had little or no flow. This material could not be used for print coatings. Further tests reproduced the results.

[0067] The reason for this result is believed to be due to the fact that in this formulation the acrylic resin has an acid number above 200 and is in solution, and precipitates with high levels of dissolved metal ions. Water-based formulations utilizing low acid number acrylic resins or acrylic emulsions, such as those described above, did not show the same instability with the metal ions.

[0068] While the 1% dispersion remained stable longer than the 2% dispersion, the 2% dispersion made with the high acid number polymer produced a precipitate which seeded out, forming an almost solid mass, which could not be easily applied to plastic film or other packaging substrates at room temperatures. The increase in metal ions, with the high level of acid groups in the soluble acrylic resin, produce this precipitation.

Example 7

[0069] On speculation that the seeding in the acrylic resin in Example 5 was due to the interaction of the silver ions with the acid groups of the acrylic resin, a 5% by weight dispersion of type AJ zeolites in sulfonated polyesters, Eastek's 1200 with acid number of 2 was made. Specifically, the formula for the dispersion of Example 6 was used except that the styrenated acrylic soluble resin and acrylic emulsion were replaced by the sulfonated polyesters.

[0070] The resultant dispersion did not seed out. Heat was applied to accelerate any precipitation or seeding and none was noted. Thus, because of their extremely low acid number, these sulfonated polyester resins may be used to create printable formulations containing 10% by weight zeolites (dry basis).

Example 8 Solvent-based Anti-microbial Dispersion Formulations

[0071] The following ingredients were used to form a solvent-based dispersion according to the present invention:

Polyamide Resin (acid No. 2) 16.40

n-Propyl Alcohol 32.80

D.I. Water 0.50

n-Propyl Alcohol 20.13

Nitrocellulose 18.00

Ethyl Acetate 3.00

Hercolyn D 3.37

Wax 3.80

AgION AJ 10D 2.00

100.00 parts by weight

[0072] The dispersion was prepared as follows:

1. 16.40 parts of polyamide resin was dissolved in 32.80 parts of n-propyl alcohol that contains 0.50 parts of de-ionized (D.I.) water with stirring.

2. A solution of 18.00 parts of nitrocellulose containing 20.13 parts of n-propanol, 3.00 Ethyl Acetate and 3.37 parts of Hercolyn D was then added to the polyamide solution and the combination was stirred well for 15 minutes.

3. Next, 2.00 parts of AgION's AJ 10 D was added to the solution under and stirred vigorously for 30 minutes.

4. The resultant mixture was passed through a horizontal mill having inert beads in the range of 0.5 – 2 mm diameter.

5. Thereafter, 3.80 parts of wax was added to the mixture and stirred for 30 minutes.

[0073] The coating was applied to polyethylene and tested for its ant-microbial properties. The test results showed that Direct Injection of the following bacteria showed a 99.9% reduction.

5	Salmonella	Staphylococcus
	E. coli	Yeast
	Pseudomonas	Mold

[0074] Many modifications and variations of this invention can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. The specific embodiments described below are offered by way of example only, and the invention is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. The various patents and publications mentioned herein are hereby incorporated herein by reference.

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